

I

THE OSMOTIC PRESSURE OF GLUCOSE
SOLUTIONS IN THE VICINITY OF
THE FREEZING POINT OF
WATER

II

THE USE OF WEIGHT-NORMAL SOLUTIONS
IN THE MEASUREMENT OF
OSMOTIC PRESSURE

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY.

BY

FRANCIS M. ROGERS.

BALTIMORE, MD.

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I.—THE OSMOTIC PRESSURE OF GLUCOSE SOLUTIONS IN THE VICINITY OF THE FREEZING POINT OF WATER.

Introduction.

This investigation on glucose solutions is a continuation of the measurement of osmotic pressure in the neighborhood of 0° . The previous work in this laboratory, on the osmotic pressure of solutions of cane-sugar¹ and of glucose,² was carried out at temperatures varying from 18° to 26° . The results obtained led to the conclusion that both cane-sugar and glucose "*in aqueous solution, at temperatures in the vicinity of 20° , exert an osmotic pressure equal to that which a molecular-equivalent quantity of a gas would exert if its volume were reduced, at the same temperature, to that of the solvent in the pure state.*"³ The fact that the pressures obtained at these temperatures are directly proportional to the concentration, indicates that these substances at the temperature of the experiments, exist in solution in the anhydrous condition.⁴ The freezing point depressions, however, have been interpreted by some as indicating that cane-sugar, at least, is hydrated in solution. This apparent contradiction may be explained by the fact that the determinations of the osmotic pressure were made at comparatively high temperatures. At these higher temperatures, the hydrates which may exist at the freezing point of the solution, may be decomposed. In order to get experimental evidence upon this, it was deemed desirable to measure the osmotic pressure of these substances at a temperature as near 0° as practicable.⁵ This would also give further experimental evidence of the application of the law of Gay-Lussac to osmotic pressure.

The first measurements at this temperature were made with cane-sugar solutions.⁶ The osmotic pressure of these solutions

¹ Am. Chem. J., **34**, 1; **36**, 39.

² Ibid., **37**, 324.

³ Ibid., **37**, 357.

⁴ Ibid., **37**, 358.

⁵ Ibid., **36**, 92.

⁶ Ibid., **37**, 425.

was found to be considerably in excess of the gas pressure calculated for the same temperature. The pressures found agreed well with the pressures calculated from the freezing point depressions, as was to be expected, since the temperature of both determinations is very nearly the same.

It was desired to determine whether glucose solutions would also give high osmotic pressures at a temperature in the vicinity of the freezing point of water. In the following will be given a description of the work on glucose solutions at this temperature and the results obtained. The general methods of procedure were the same as those previously employed.¹ Some few details have been changed and these will be brought out in the proper place.

The Constant-Temperature Bath.

For maintaining a constant temperature, one of the large tanks that were installed last year was employed. This tank is entirely similar in construction to the one that has been described in detail elsewhere² and it has not been thought necessary to go into its description here. However, it had to be modified in order to obtain temperatures in the neighborhood of 0°, and a description of how this was accomplished should be given.

It may be well to recall that the bath consists essentially of two parts: (1) a large tank containing about 300 liters of water, (2) an enclosed air space above. Both the air and water are kept in constant circulation by means of mechanical stirrers. The air is drawn from the top of the enclosed space through long pipes which lie in the water near the bottom of the tank. This is done to maintain the air as nearly as possible at the same temperature as the water.

The ice necessary to obtain the low temperature is contained in large cans of galvanized sheet-iron. One of these cans is placed in each end of the tank. They extend nearly to the bottom of the water and are supported by flanges at the top on the edges of the tank. The dimensions of these cans are 28 cm. by 40 cm. by 59 cm. They are fitted with holes in the bottom and on the sides near the top, but beneath the surface of the water.

¹ Am. Chem. J., 34, 1; 36, 1; 36, 39.

² Ibid., 36, 1.

These holes permit free circulation of the water through the ice, and at the same time afford a means of escape for the water from the melting of the ice.

To facilitate the maintenance of a low temperature in the air, the cans are extended up 40 cm., in sections, nearly to the top of the enclosed air space. At the top these sections are joined by two shallow pans, placed beside each other. By this means the whole top of the air space can be filled with ice. The air in the tank is thus surrounded on two sides and on the top with ice, and a temperature sufficiently near that of the water is easily obtained. The cans when completely filled hold about 375 pounds of ice.

The tank is provided at one end with a constant-level siphon for the overflow of the water as the ice melts. The water is collected below in a small tank, on the outside of which is a gauge graduated to read in pounds of water. By this means the amount of ice that melts in 24 hours is easily obtained. It was found that an average of about 20 pounds per day melted.

Between the ice cans an iron plate rests on the edges of the tank. This supports two cans, which extend far beneath the surface of the water, and into which the bottles containing the cells are put. In order to insure that the solution in the cell will come quickly to the temperature of the water in the tank, enough water is kept in the bottom of the cans to just come up to the top of the bottle.

To prevent the entrance of outside air into the tank, all the cracks are covered with adhesive plaster. The house which encloses the air space above the water is covered on all exposed sides with heavy pads lined with hair. The room, in which the tank is situated, is small and is not used for any other purpose. Hence it was possible to cut the heat off from the room and to keep the windows open.

The temperature of the water remained very nearly constant, independent of the outside temperature. Only in one case did it get above $0^{\circ}.3$. The temperature of the air, however, varied considerably with the external temperature. Toward the last of the work, warm weather necessitated putting in an

additional ice box in the back of the tank. With this in place there was room for the accommodation of but one cell.

Table A is a record of the temperatures obtained during this series of measurements and shows with what effectiveness the above arrangement worked, and what constancy of temperature was maintained. Columns 1 and 2 need no explanation. Column 3 gives the temperature of the water, *i. e.*, of the solution in the cell. The temperatures given are the averages of the several temperatures observed after a maximum pressure was reached. The temperatures in column 4 are also averages of several readings taken at the same time as the temperatures of the water. In columns 5 and 6 are given the differences between the lowest and highest temperatures in the water and

Table A.

Wt. normal conc.	No. of exp.	Tempera- ture of the water.	Tempera- ture of the air.	Change of tempera- ture in the water.	Change of tem- perature in the air.	Time during which temperature was meas- ured. Hours.
1.	2.	3.	4.	5.	6.	7.
0.1	1	0°.28	1°.00	0°.23	0°.31	16
	2	0°.24	0°.66	0°.10	0°.20	17
0.2	1	0°.12	0°.74	0°.02	0°.15	14
	2	0°.13	0°.79	0°.02	0°.12	17
0.3	1	0°.19	0°.96	0°.08	0°.04	16
	2	0°.22	0°.60	0°.09	0°.14	19
0.4	1	0°.12	0°.82	0°.02	0°.21	20
	2	0°.21	0°.65	0°.11	0°.18	18
0.5	1	0°.17	0°.86	0°.07	0°.12	19
	2	0°.24	0°.66	0°.15	0°.14	16
0.6	1	0°.12	0°.76	0°.06	0°.07	17
	2	0°.08	0°.45	0°.00	0°.11	20
0.7	1	0°.08	0°.48	0°.04	0°.12	15
	2	0°.06	0°.49	0°.00	0°.03	10
0.8	1	0°.13	0°.78	0°.03	0°.13	17
	2	0°.13	0°.77	0°.03	0°.13	20
0.9	1	0°.16	0°.93	0°.14	0°.37	18
	2	0°.15	0°.90	0°.14	0°.37	21
1.0	1	0°.17	0°.86	0°.10	0°.33	17
	2	0°.17	0°.89	0°.10	0°.33	17

the air, respectively. The greatest change in the temperature of the water is shown to be $0^{\circ}.23$, the change lasting over 16 hours. Column 7 shows the time in hours during which the temperatures were measured. This, also, is the time a maximum pressure was maintained before taking the cell down.

A few other data, not shown in the table, may be given. The average temperature of the water was $0^{\circ}.16$, and of the air, $0^{\circ}.64$. The maximum difference in temperature between the water and the air was $0^{\circ}.91$, and the minimum, $0^{\circ}.30$, the average being $0^{\circ}.48$. With such constancy of temperature, there was no fear of the so-called "thermometer effects."¹

The Cells.

The cells used in this work are designated by the letters B, D and G. They are of the same form as those previously described.² The membrane used was of copper ferrocyanide, deposited electrolytically by the method of Morse and Horn.³

Since the expansion and contraction of the cell upon repeated changes in temperature are apt to loosen the membrane, it was found advisable to keep the cells always as near 0° as possible. When not in use they were kept in water surrounded by ice. During the deposition of the membrane, the solution of copper sulphate was immersed in an ice bath. The solution of potassium ferrocyanide was also kept cold.

At the temperature thus obtained, which was about 2° , the membranes showed a much higher resistance than at ordinary temperatures. Thus, these cells, which gave a maximum resistance of from 100,000 to 130,000 ohms when the membrane was deposited at the temperature of the laboratory, at this low temperature gave a resistance usually amounting to 550,000 ohms.

All three of these cells were used in a series of measurements on cane-sugar solutions carried out this year, but for three weeks just before the commencement of this work they were not in actual use. During this time the membranes were deposited every day. As the membranes are strengthened by each de-

¹ Am. Chem. J., **34**, 23.

² Ibid., **34**, 11.

³ Ibid., **26**, 80.

position, they were in excellent condition, and there is no doubt that maximum pressures were obtained.

Cell B was used only with dilute solutions, and even here it did not appear to give maximum pressures. It is a fact, as noticed in this laboratory, that some cells, which give maximum pressures with cane-sugar, do not with glucose. However, in the case of the 0.6 normal solution, this cell did give a maximum pressure.

The other two cells were used throughout the series. They both gave the same maximum pressures, as was shown by comparing them on solutions of the same concentration. For example, with the 0.8 normal solution, G gave a maximum pressure of 18.87 atmospheres and D, 18.90 atmospheres. These cells are remarkable for the short time required for them to reach a maximum pressure, six hours being about the average.

The Manometers.

Two manometers, with the laboratory numbers, 20 and 21, were employed. They are of the same form as those used in previous work and require no description here.¹

One of the great troubles in the earlier work here was the slipping of the manometer through the stopper during a measurement. This has been practically overcome in the following way:

The rubber stopper, which is put on the manometer with a solution of rubber in carbon bisulphide, is wrapped very tightly with waxed shoemaker's thread, just around the lower end. This prevents the enlargement on the end of the manometer from slipping up into the stopper. After the stopper has been inserted into the cell as far as possible, the part still protruding above is wrapped closely and very tightly with heavy waxed thread. When the stopper is thus wrapped it is perfectly rigid and can not expand under the subsequent pressure in the cell. This method of tying the stopper has proved very satisfactory. For example, in the series of measurements on cane-sugar in the neighborhood of 20°, the displacement of the manometer varied from 0.07 mm. to 3.78 mm., the mean being 0.95 mm.² The stoppers were not tied around the bottom. In this series the greatest displacement was 0.34 mm., and the average, 0.1 mm. (see Table XXI.).

¹ Am. Chem. J., 34, 11; 36, 20.

² Ibid., 36, 53.

Table B.—Data for Calibration of Manometer No. 20.

Readings upward on scale.	Differences.	Readings on scale calcu- lated from zero point.	Product of number of settings by mean space filled.	Correction values.
1	2	3	4	5
875.65				
863.26	12.39	12.39	12.478	+0.088
850.87	12.39	24.78	24.956	+0.176
838.48	12.39	37.17	37.434	+0.264
826.10	12.38	49.55	49.912	+0.362
813.72	12.38	61.93	62.390	+0.460
801.35	12.37	74.30	74.868	+0.568
788.97	12.38	86.68	87.346	+0.666
776.60	12.37	99.05	99.824	+0.774
764.23	12.37	111.42	112.302	+0.882
751.86	12.37	123.79	124.780	+0.990
739.49	12.37	136.16	137.258	+1.098
727.11	12.38	148.54	149.736	+1.196
714.71	12.40	160.94	162.214	+1.274
702.30	12.41	173.35	174.692	+1.342
689.88	12.42	185.77	187.170	+1.400
677.45	12.43	198.20	199.648	+1.448
665.00	12.45	210.65	212.126	+1.476
652.54	12.46	223.11	224.604	+1.494
640.07	12.47	235.58	237.082	+1.502
627.58	12.49	248.07	249.560	+1.490
615.05	12.53	260.60	262.038	+1.438
602.50	12.55	273.15	274.516	+1.366
589.92	12.58	285.73	286.994	+1.264
577.33	12.59	298.32	299.472	+1.152
564.73	12.60	310.92	311.950	+1.030
552.13	12.60	323.52	324.428	+0.908
539.54	12.59	336.11	336.906	+0.796
526.96	12.58	348.69	349.384	+0.694
514.39	12.57	361.26	361.862	+0.602
501.84	12.55	373.81	374.340	+0.530
489.30	12.54	386.35	386.818	+0.468
476.77	12.53	398.88	399.296	+0.416
464.24	12.53	411.41	411.774	+0.364
451.71	12.53	423.94	424.252	+0.312
439.18	12.53	436.47	436.730	+0.260
426.65	12.53	449.00	449.208	+0.208
414.12	12.53	461.53	461.686	+0.156
401.60	12.52	474.05	474.164	+0.114
389.08	12.52	486.57	486.642	+0.072
376.56	12.52	499.09	499.120	+0.030
364.04	12.52	511.61	511.598	—0.012

These manometers were calibrated with the greatest possible care.¹ Table B contains the calibration data for manometer No. 20.² Other data necessary for the use of these manometers are as follows:

Manometer No. 20.

Mean diameter of bore	0.45	mm.
Correction for double meniscus	0.15	mm.
Distance from scratch No. 1 to top of manometer	475.53	mm.
No. of calibration units of air, under standard conditions, contained in manometer	495.09	
Capillary depression	0.02	atmos.

Manometer No. 21.

Mean diameter of bore	0.69	mm.
Correction for double meniscus	0.23	mm.
Distance from scratch No. 1 to top of manometer	408.20	mm.
No. of calibration units of air, under standard conditions, contained in manometer	478.16	
Capillary depression	0.02	atmos.

The manometers compared well with each other. They were used indiscriminately with either cell and on the same concentration registered practically identical pressures.

The manometers were filled with pure, dry air and sealed in such a manner as to leave a short thread of mercury at the top. The method by which this is accomplished has been described by Morse and Frazer.³

The mercury used in the manometers was most carefully purified by being sprayed through a column of dilute nitric acid. This process of purification was continued for several weeks. After washing and drying, it was kept in a separatory funnel under sulphuric acid. If the mercury contains even a trace of amalgam, it will in time be oxidized, thus causing a decrease in the volume of the air contained in the manometer. To ascertain whether any such decrease had taken place in the manometers during the course of the work, the air volumes were redetermined at the completion of the measurements. No

¹ Am. Chem. J., 34, 6.

² For the calibration data of manometer No. 21, see W. W. Holland, Dissertation, Johns Hopkins University (1907).

³ Am. Chem. J., 36, 21.

change of volume was found in manometer No. 21. No. 20, however, showed a slight decrease. This determination was not made for some time after the manometer had been used, and since the results obtained with it agreed with those of No. 21 throughout the work, it was not thought advisable to apply any correction for the decrease in volume.

The Material.

The glucose that was obtained for this work is known to the trade as "Traubenzucker Kahlbaum." It was hoped that this would be of sufficient purity to use at once, but on investigation it was found to have a melting point which was not at all sharp. Pure glucose melts at 146° while this gave an indefinite melting point of about 143° . It also contained a trace of alcohol, as shown by the "iodoform test." Its complete analysis gave:

	Found Per cent.	Theoretical. Per cent.
Carbon.....	40.31	39.98
Hydrogen.....	6.64	6.71

A standard solution was made for the purpose of testing its rotation, as directed by Landolt.¹ For this purpose 32.63 grams (32.65 grams corrected for air displacement) were dissolved in water and set aside for 24 hours until the birotation had ceased. The solution was then diluted to 100 cc. at 17.5° . A solution of pure glucose made up in this manner gives a rotation of 100 degrees in a two-decimeter tube. The rotation found, however, was 101.5 degrees. It was thought that this glucose might contain dextrin, due to incomplete hydrolysis in its preparation. But it gave no pink color with iodine, which is quite a delicate test for dextrin, and showed no loss in rotation after the addition of hydrochloric acid.

This "Traubenzucker," together with some glucose, which had been used previously in determinations of freezing points and density, was purified by four precipitations from a hot and concentrated solution with strong alcohol, heated nearly to the boiling point. Under these conditions glucose comes out of

¹ H. Landolt: Das Optische Drehungsvermögen, 2nd Auflage, p. 448.

solution in the anhydrous form. It was then thoroughly washed with alcohol and dried in a vacuum desiccator over sulphuric acid to a constant weight. The sulphuric acid served the double purpose of removing the alcohol and at the same time dehydrating any hydrated glucose that might have been present.

The glucose thus purified contained a very minute trace of alcohol. It melted more sharply, between 145° and 146° . Its standard solution, prepared as indicated above, had a rotation of 100.5 degrees. Its complete analysis gave:

	Found. Per cent.	Theoretical. Per cent.
Carbon.....	40.03	39.98
Hydrogen.....	6.72	6.71

This was then considered to be of such a degree of purity as to warrant its use.

The Preparation of the Solutions.

All the solutions were made up on the weight-normal basis, that is, one gram-molecule ($H=1$) or fraction thereof was dissolved in 1000 grams of water. The weights were all corrected for air displacement. The solutions of glucose on the inside of the cell were made 0.01 ion-normal with potassium ferrocyanide, and the water on the outside was also made 0.01 ion-normal with copper sulphate. These "membrane-formers" are found necessary to patch up any small rent in the membrane that may take place. This is most apt to occur during the closing or opening of the cell, when the pressure is suddenly put on and removed from the membrane.

These solutions were made up on the assumption that potassium ferrocyanide dissociates into five ions and copper sulphate into two. If this assumption be correct, the solutions on the two sides of the membrane would be isotonic in respect to the "membrane-formers." However, some recent work of Jones and Bassett¹ on the depression of the freezing points of solutions of potassium ferrocyanide point to the conclusion that this substance dissociates into eight instead of five ions. If this be true, the pressures measured are slightly high. Some measurements made in this laboratory on the osmotic pressure of the "membrane-formers" alone, also apparently show that a slight correction

¹ Am. Chem. J., 34, 311.

should be applied for the osmotic inequality of the ferrocyanide and sulphate solutions. However, since this point has not been definitely settled as yet, the solutions were made up on the original assumption.

In the preliminary work on the osmotic pressure of glucose solutions, it was soon noticed that the solutions became infected with a growth of *penicillium*. This would bring about chemical changes in the glucose and also would probably affect the efficiency of the membrane. A series of experiments was carried out to find a poison for this *penicillium*.¹ Of several poisons tried, thymol was found to be the most satisfactory. Hence, to prevent the appearance of this fungus, all the solutions were made up 0.001 normal with thymol. Since the solution in the cell and that on the outside were of the same concentration in regard to thymol, this obviously did not effect the pressures.

Corrections.

The chief correction that has to be applied is for the dilution of the cell contents. This is due either to the inflow of water or to leakage of the dissolved substance through the membrane. The latter source of dilution, however, is excluded by the great care taken to perfect the membranes, and by the fact that no glucose has been detected in the solution on the outside of the cell.

The amount of dilution was determined polariscopically. The instrument used is a Schmidt and Haensch half-shadow polariscope, with triple field and double wedge compensation. The source of light is a small incandescent lamp and a uniform field is obtained by passing the light through a solution of potassium bichromate. The rotations were taken in two-decimeter tubes after the solutions had been made up at least 24 hours. This time is required for the birotation to cease. The rotation of the original solution, as made up, was taken and that of the solution from the cell at the completion of the experiment. The loss in rotation, due to dilution, was calculated as percentage loss and the corresponding correction applied to the pressures found.

¹ Am. Chem. J., 36, 36.

The question of dilution, and whether all the dilution, as shown by the loss in rotation, takes place during the time that the cell is "up" and while observations are being made on the pressure, is quite a complicated one. After the cell has been closed, pressure is brought to bear upon the cell contents mechanically until the mercury rises in the manometer to a position almost corresponding to the maximum pressure. Under these conditions only a very slight amount of water can enter the cell while observations are being taken, especially since the slipping of the manometer has been practically overcome.

Dilution, however, may take place at two other times, either during the closing or the opening of the cell.

To overcome these sources of dilution, the cell was dipped in a solution of the same concentration as the one in the cell, just before the beginning of these operations. With the concentrated solutions, even stronger dipping solutions were used. The cell, of course, was thoroughly washed off before putting into the bottle containing the outside solution of copper sulphate. This method of procedure served to greatly diminish the dilution.

When the cell is being closed, the forcing-in of the stopper keeps the cell contents continually under pressure. But when the cell is being opened, at the conclusion of the experiment, the pulling-out of the stopper keeps the cell contents under diminished pressure. Hence it is probable that more dilution takes place during the latter operation than during the former, notwithstanding the fact that less time is required. The average time that was required to close a cell was eleven minutes, and to open, three minutes. The dilution that occurs during the opening of a cell is measured, by loss in rotation, along with the dilution that takes place previously. But this dilution, of course, does not affect the pressure as observed, since it takes place afterwards. From these considerations it is quite certain that at least half the dilution occurs while the cell is being opened and hence should not be included in the correction for dilution. Table XXIV. contains the pressures found where only half the loss in rotation is employed in correcting for dilution.

There is one other source of dilution that should be mentioned. If the cell and its contents are at the temperature of the room

when the cell is put into the bath, the contraction of the cell contents will permit the entrance of water. For this reason all the solutions used, as well as the cell, were cooled in an ice bath before the operation of closing the cell.

Besides this correction for dilution, other corrections were applied, for the capillary depression of the mercury, for the double meniscus, for the liquids in the manometer and for variations in atmospheric pressure.¹ A slight correction should probably be applied for the osmotic inequality of the "membrane-formers," as pointed out above. This correction however, has not been applied, since its exact value has not been determined.

Experimental Results.

Tables I. to XX., inclusive, contain the results of the individual experiments. Although the actual readings as made, are not given, the tables are sufficiently full to permit of a recalculation of the pressures if so desired. At the foot of each table is given a short summary of the results of that particular experiment. The summary includes the following:

The total displacement of the manometer during the experiment.

The dilution correction, in atmospheres, corresponding to the whole loss in rotation and also to one-half the loss in rotation.

The osmotic pressure, the molecular osmotic pressure and the ratio of osmotic to gas pressure, obtained by applying each of the above corrections for dilution.

The ratio of Δ to 1.85, Δ being the observed molecular lowering of the freezing point, which is practically a constant, 1.92,¹ and was taken as such in calculating this ratio.

¹ Am. Chem. J., 36, 44.

² Ibid., 37, 360.

Table I.

Original wt. normal concentration of solution, 0.1.	Experiment No. 1.																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																												
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0° 28 Displacement of the manometer = 0.04 mm.

Results, if corrected for whole loss in rotation: Results, if corrected for half the loss in rotation:

Correction = 0.01 atmosphere. Correction = 0.005 atmosphere.

Osmotic pressure = 2.40 atmospheres. Osmotic pressure = 2.39 atmospheres.

Molecular pressure = 23.95 atmospheres. Molecular pressure = 23.90 atmospheres.

Ratio of osmotic to gas pressure = 1.074. Ratio of osmotic to gas pressure = 1.072.

Ratio of Δ to 1.85 = 1.038.

Original wt. normal concentration of solution, 0.1. Experiment No. I.
 Rotation of original solution, 5° 22. Manometer used No. 20.
 Rotation at conclusion of experiment, 5° 20. Capillary depression, 0.02.
 Loss in concentration, 0° 02 = 0.38 per cent. Cell used, D.
 Calibration units of air in manometer, 495.09. Resistance of membrane, 546,000.
 Time of setting up cell, 4.00 P.M., March 13, 1907. Initial pressure, 1.43 atmospheres.

Table II.

Original wt. normal concentration of solution, 0.1. Experiment No. 2.
 Rotation of original solution, 5°.22. Manometer used, No. 21.
 Rotation at conclusion of experiment, 5°.22. Capillary depression, 0.02.
 Loss in concentration, 0°.00. Cell used, G.
 Calibration units of air in manometer, 478.16. Resistance of membrane, 550,000.
 Time of setting up cell, 3.30 P.M., March 14, 1907. Initial pressure, 2.13 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Difference between pressure found and calculated.		
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.		Osmotic pressure corrected.	Theoretical gas pressure.
March 14											
5.00 P.M.	0°.22	4°.80	176.62								
7.45 "	0°.20	0°.87	163.50								
11.15 "	0°.18	0°.69	159.08	158.68	1.00	0.37	0.00	0.02	2.40	2.23	0.17
March 15											
10.00 A.M.	0°.24	0°.57	158.43	158.10	1.01	0.37	0.00	0.02	2.40	2.23	0.17
12.30 P.M.	0°.25	0°.63	158.44	158.07	1.01	0.37	0.00	0.02	2.40	2.23	0.17
4.15 "	0°.28	0°.77	158.47	158.02	1.01	0.37	0.00	0.02	2.41	2.23	0.18
	0°.24										

Displacement of manometer = 0.17 mm.

Displacement of manometer = 0.17 mm.

Results, if corrected for whole loss in rotation: Results, if corrected for half the loss in rotation:

Correction = 0.00.

Osmotic pressure = 2.40 atmospheres.

Molecular pressure = 24.03 atmospheres.

Ratio of osmotic to gas pressure = 1.077.

Correction = 0.00.

Osmotic pressure = 2.40 atmospheres.

Molecular pressure = 24.03 atmospheres.

Ratio of osmotic to gas pressure = 1.077.

Ratio of Δ to 1.85 = 1.038.

Table III.

Original wt. normal concentration of solution, 0.2. Experiment No. 1.
 Rotation of original solution, $10^{\circ}.4$. Manometer used, No. 6.
 Rotation at conclusion of experiment, $10^{\circ}.3$. Capillary depression, 0.02.
 Loss in concentration, $0^{\circ}.1 = 0.96$ per cent. Cell used, G.
 Calibration units of air in manometer, 396.89. Resistance of membrane, 543,000.
 Time of setting up cell, 4.30 P.M., Feb. 15, 1907. Initial pressure, 4.30 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.			Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	
Feb. 15								
6.00 P.M.	$0^{\circ}.12$	$1^{\circ}.40$	85.08					
9.00 "	$0^{\circ}.10$	$0^{\circ}.79$	79.87	79.64	1.00	0.60	0.05	4.65 4.45 0.20
11.30 "	$0^{\circ}.12$	$0^{\circ}.72$	79.75	79.54	1.00	0.60	0.05	4.66 4.45 0.21
Feb. 16								
8.30 A.M.	$0^{\circ}.12$	$0^{\circ}.64$	79.71	79.52	1.00	0.60	0.05	4.66 4.45 0.21
11.30 "	$0^{\circ}.12$	$0^{\circ}.79$	79.75	79.52	1.00	0.60	0.05	4.66 4.45 0.21

$0^{\circ}.12$ Displacement of manometer = 0.05 mm.

Results, if corrected for whole loss in rotation:
 Correction = 0.05 atmosphere.

Osmotic pressure = 4.66 atmospheres.

Molecular pressure = 23.29 atmospheres.

Ratio of osmotic to gas pressure = 1.047.

Results, if corrected for half the loss in rotation:
 Correction = 0.025 atmosphere.

Osmotic pressure = 4.63 atmospheres.

Molecular pressure = 23.16 atmospheres.

Ratio of osmotic to gas pressure = 1.041.

Ratio of Δ to 1.85 = 1.038.

Table IV.

Original wt. normal concentration of solution, 0.2
 Rotation of original solution, $10^{\circ}50$.
 Rotation at conclusion of experiment, $10^{\circ}45$.
 Loss in concentration, $0^{\circ}05 = 0.48$ per cent.
 Calibration units of air in manometer, 495.09.
 Time of setting up cell, 3.45 P.M., Feb. 19, 1907.

Experiment No. 2.
 Manometer used, No. 20.
 Capillary depression, 0.02.
 Cell used, D.

Resistance of membrane, 502,500.
 Initial pressure, 4.07 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.			Difference between pressure found and calculated.
	Solution.	Air in ether.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	
Feb. 19								
5.45 P.M.	$0^{\circ}12$	$2^{\circ}60$	110.03	108.99				
8.00 "	$0^{\circ}12$	$0^{\circ}96$	98.08	97.73				
11.00 "	$0^{\circ}12$	$0^{\circ}87$	97.44	97.13	0.99	0.52	0.03	4.68 4.45 0.23
Feb. 20								
10.00 A.M.	$0^{\circ}14$	$0^{\circ}75$	97.48	97.21	0.99	0.52	0.03	4.67 4.45 0.22
1.00 P.M.	$0^{\circ}14$	$0^{\circ}75$	97.43	97.16	0.99	0.52	0.03	4.68 4.45 0.23
4.15 "	$0^{\circ}12$	$0^{\circ}79$	97.45	97.17	0.99	0.52	0.03	4.68 4.45 0.23
	$0^{\circ}13$							

Displacement of manometer = 0.04 mm.

Results, if corrected for whole loss in rotation: Results, if corrected for half the loss in rotation:

Correction = 0.03 atmosphere.

Osmotic pressure = 4.68 atmospheres.

Molecular pressure = 23.39 atmospheres.

Ratio of osmotic to gas pressure = 1.051.

Correction = 0.015 atmosphere.

Osmotic pressure = 4.66 atmospheres.

Molecular pressure = 23.31 atmospheres.

Ratio of osmotic to gas pressure = 1.048.

Ratio of d to $1.85 = 1.038$.

Table V.

Original wt. normal concentration of solution, 0.3.	Experiment No. 1.																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																	
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Displacement of manometer = 0.16 mm.

Results, if corrected for whole loss in rotation:

Correction = 0.05 atmospheres.

Osmotic pressure = 7.04 atmospheres.

Molecular pressure = 23.45 atmospheres.

Ratio of osmotic to gas pressure = 1.054.

Results, if corrected for half the loss in rotation:

Correction = 0.025 atmospheres.

Osmotic pressure = 7.01 atmospheres.

Molecular pressure = 23.38 atmospheres.

Ratio of osmotic to gas pressure = 1.050.

Ratio of Δ to 1.85 = 1.038.

Original wt. normal concentration of solution, 0.3.
 Rotation of original solution, 15°.65.
 Rotation at conclusion of experiment, 15°.55.
 Loss in concentration, 0°.10 = 0.64 per cent.
 Calibration units of air in manometer, 478.16.
 Time of setting up cell, 12.30 P.M., Feb. 16, 1907.
 Resistance of membrane, 595,000.
 Initial pressure, 5.91 atmospheres.

Experiment No. 1.
 Manometer used, No. 21.
 Capillary depression, 0.02.
 Cell used, D.
 Resistance of membrane, 595,000.
 Initial pressure, 5.91 atmospheres.

Table VI.

Original wt. normal concentration of solution, 0.3. Experiment No. 2.
 Rotation of original solution, $15^{\circ} 53$. Manometer used, No. 21.
 Rotation at conclusion of experiment, $15^{\circ} 42$. Capillary depression, 0.02.
 Loss in concentration, $0^{\circ} 11 = 0.71$ per cent. Cell used, G.
 Calibration units of air in manometer, 478.16. Resistance of membrane, 368,000.
 Time of setting up cell, 3.45 P.M., March 18, 1907. Initial pressure, 5.83 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Difference between theoretical gas pressure pres- found and sure, calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.		
March 18										
4.45 P.M.	0°.18	5°.00	76.96	75.57						
8.00 "	0°.17	0°.69	64.18	64.02	1.01	0.50	0.06	0.02	7.04	6.68 0.36
11.00 "	0°.18	0°.60	64.15	64.01	1.01	0.50	0.06	0.02	7.04	6.68 0.36
March 19										
10.15 A.M.	0°.23	0°.55	64.18	64.05	1.00	0.50	0.06	0.02	7.05	6.68 0.37
12.30 P.M.	0°.25	0°.55	64.20	64.07	1.00	0.50	0.06	0.02	7.04	6.69 0.35
3.00 "	0°.26	0°.60	64.20	64.06	0.99	0.50	0.06	0.02	7.05	6.69 0.36
	0°.22									

Displacement of manometer = 0.15 mm.

Results, if corrected for whole loss in rotation: Displacement of manometer = 0.15 mm.
 Correction = 0.06 atmosphere. Results, if corrected for half the loss in rotation:
 Osmotic pressure = 7.04 atmospheres. Correction = 0.03 atmosphere.
 Molecular pressure = 23.48 atmospheres. Osmotic pressure = 7.01 atmospheres.
 Ratio of osmotic to gas pressure = 1.054. Molecular pressure = 23.37 atmospheres.
 Ratio of osmotic to gas pressure = 1.049. Ratio of Δ to 1.85 = 1.038.

Table VII.

Original wt. normal concentration of solution, 0.4.	Experiment No. 1.																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																											
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Displacement of manometer = 0.00.

Results, if corrected for whole loss in rotation:
Correction = 0.08 atmosphere.

Results, if corrected for half the loss in rotation:
Correction = 0.04 atmosphere.

Osmotic pressure = 9.35 atmospheres.

Osmotic pressure = 9.31 atmospheres.

Molecular pressure = 23.37 atmospheres.

Molecular pressure = 23.27 atmospheres.

Ratio of osmotic to gas pressure = 1.049.

Ratio of osmotic to gas pressure = 1.045.

Ratio of λ to 1.85 = 1.038.

Original wt. normal concentration of solution, 0.4.
Rotation of original solution, 20°.65.
Rotation at conclusion of experiment, 20°.50.
Loss in concentration, 0°.15 = 0.73 per cent.
Calibration units of air in manometer, 478.16.
Time of setting up cell, 4.30 P.M., Feb. 18, 1907.
Resistance of membrane, 434,000.
Initial pressure, 9.09 atmospheres.

Experiment No. 1.

Manometer used, No. 21.

Capillary depression, 0.02.

Cell used, G.

Table VIII.

Original wt. normal concentration of solution, 0.4. Experiment No. 2.
 Rotation at original solution, $20^{\circ}.58$. Manometer used, No. 20.
 Rotation at conclusion of experiment, $20^{\circ}.40$. Capillary depression, 0.02.
 Loss in concentration, $0^{\circ}.18 = 0^{\circ}.87$ per cent. Cell used, D.
 Calibration units of air in manometer, 495.09. Resistance of membrane, 360,000.
 Time of setting up cell, 4.00 P.M., March 15, 1907. Initial pressure, 7.25 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.			Theoretical gas pressure found and calculated.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Osmotic pressure corrected.	
March 15									
5.15 P.M.	$0^{\circ}.22$	$4^{\circ}.60$	65.69	64.59					
7.30 "	$0^{\circ}.20$	$0^{\circ}.80$	51.98	51.83					
11.00 "	$0^{\circ}.19$	$0^{\circ}.69$	51.46	51.33	1.01	0.58	0.09	9.33	8.91 0.42
March 16									
8.45 A.M.	$0^{\circ}.14$	$0^{\circ}.54$	51.39	51.29	1.01	0.58	0.09	9.33	8.91 0.42
5.00 P.M.	$0^{\circ}.30$	$0^{\circ}.72$	51.46	51.32	1.01	0.58	0.09	9.33	8.92 0.41
	$0^{\circ}.21$								

Displacement of manometer = 0.34 mm.

Results, if corrected for whole loss in rotation:

Correction = 0.09 atmosphere.

Osmotic pressure = 9.33 atmospheres.

Molecular pressure = 23.33 atmospheres.

Ratio of osmotic to gas pressure = 1.047.

Results, if corrected for half the loss in rotation:

Correction = 0.045 atmosphere.

Osmotic pressure = 9.29 atmospheres.

Molecular pressure = 23.21 atmospheres.

Ratio of osmotic to gas pressure = 1.042.

Ratio of 4 to 1.85 = 1.038.

Table IX.

Original wt. normal concentration of solution, 0.5.
 Rotation of original solution, $25^{\circ} .55$.
 Rotation at conclusion of experiment, $25^{\circ} .40$.
 Loss in concentration, $0^{\circ} .15 = 0.58$ per cent.
 Calibration units of air in manometer, 495.09.
 Time of setting up cell, 4.15 P.M., Mar. 11, 1907.

Time.	Temperature.		Volume of air in manometer.		Corrections.			Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Corrected.		Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.			
			Uncorrected.	Corrected.						
March 11										
5.15 P.M.	0° .24	2° .30	48.10	47.70						
8.00 "	0° .17	0° .94	41.40	41.26	1.01	0.60	0.07	0.02	11.68	11.14
11.45 "	0° .12	0° .85	41.32	41.19	1.01	0.60	0.07	0.02	11.70	11.14
March 12										
10.00 A.M.	0° .17	0° .72	41.35	41.24	1.01	0.60	0.07	0.02	11.69	11.14
12.45 P.M.	0° .19	0° .86	41.35	41.21	1.00	0.60	0.07	0.02	11.70	11.14
3.30 "	0° .18	0° .94	41.36	41.22	1.00	0.60	0.07	0.02	11.70	11.14

$0^{\circ} .17$ Displacement of manometer = 0.18 mm.

Results, if corrected for whole loss in rotation:

Correction = 0.07 atmosphere.

Osmotic pressure = 11.69 atmospheres.

Molecular pressure = 23.39 atmospheres.

Ratio of osmotic to gas pressure = 1.050.

Results, if corrected for half the loss in rotation:

Correction = 0.035 atmosphere.

Osmotic pressure = 11.66 atmospheres.

Molecular pressure = 23.32 atmospheres.

Ratio of osmotic to gas pressure = 1.047.

Ratio of 1 to 1.85 = 1.038.

Table XI.

Original wt. normal concentration of solution, 0.6. Experiment No. 1.
 Rotation of original solution, 30°.65. Manometer used, No. 21.
 Rotation at conclusion of experiment, 30°.10. Capillary depression, 0.02.
 Loss in concentration, 0°.55 = 1.47 per cent. Cell used, B.
 Calibration units of air in manometer, 478.16. Resistance of membrane, 547,000.
 Time of setting up cell, 4.00 P.M., Feb. 20, 1907. Initial pressure, 12.93 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Atmospheric pressure.	Corrections.			Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.		Liquids in manometer.	Dilution of cell contents.	Capillary depression.		
Feb. 20										
5.30 P.M.	0°.12	1°.60	35.96	35.75						
7.30 "	0°.10	0°.86	33.58	33.47						
11.15 "	0°.08	0°.79	33.45	33.35	0.99	0.54	0.22	0.02	14.13	0.77
Feb. 21										
10.15 A.M.	0°.12	0°.72	33.52	33.43	0.99	0.54	0.22	0.02	14.09	0.73
1.00 P.M.	0°.14	0°.79	33.47	33.37	0.99	0.54	0.22	0.02	14.12	0.76
4.30 "	0°.14	0°.73	33.46	33.37	0.99	0.54	0.22	0.02	14.12	0.76

0°.12 Displacement of manometer = 0.06 mm.

Results, if corrected for whole loss in rotation: Results, if corrected for half the loss in rotation:

Correction = 0.22 atmosphere.

Correction = 0.11 atmosphere.

Osmotic pressure = 14.12 atmospheres.

Molecular pressure = 23.34 atmospheres.

Ratio of osmotic to gas pressure = 1.048.

Ratio of Δ to 1.85 = 1.038.

Table XII.

Original wt. normal concentration of solution, 0.6. Experiment No. 2.
 Rotation of original solution, $30^{\circ} 55'$. Manometer used, No. 21.
 Rotation at conclusion of experiment, $30^{\circ} 10'$. Capillary depression, 0.02.
 Loss in concentration, $0^{\circ} 45' = 1.47$ per cent. Cell used, G.
 Calibration units of air in manometer, 478.16. Resistance of membrane, 545,000.
 Time of setting up cell, 4.15 P.M., Feb. 22, 1907. Initial pressure, 13.64 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Atmospheric pressure.	Corrections.		Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.		Liquids in manometer.	Dilution of cell contents.			
Feb. 22										
5.30 P.M.	$0^{\circ} 06'$	$1^{\circ} 40'$	34.17	33.96						
8.00 "	$0^{\circ} 08'$	$0^{\circ} 49'$	33.37	33.31	1.02	0.54	0.22	0.02	14.11	0.75
11.30 "	$0^{\circ} 08'$	$0^{\circ} 43'$	33.30	33.25	1.02	0.54	0.22	0.02	14.14	0.78
Feb. 23										
10.30 A.M.	$0^{\circ} 08'$	$0^{\circ} 39'$	33.33	33.28	1.03	0.54	0.22	0.02	14.11	0.75
1.00 P.M.	$0^{\circ} 08'$	$0^{\circ} 46'$	33.36	33.30	1.02	0.54	0.22	0.02	14.11	0.75
4.30 "	$0^{\circ} 08'$	$0^{\circ} 50'$	33.36	33.30	1.02	0.54	0.22	0.02	14.11	0.75
	$0^{\circ} 08'$									

Displacement of manometer = 0.00.

Results, if corrected for whole loss in rotation: Results, if corrected for half the loss in rotation:

Correction = 0.22 atmosphere.

Osmotic pressure = 14.12 atmospheres.

Molecular pressure = 23.53 atmospheres

Ratio of osmotic to gas pressure = 1.057.

Correction = 0.11 atmosphere.

Osmotic pressure = 14.01 atmospheres.

Molecular pressure = 23.34 atmospheres.

Ratio of osmotic to gas pressure = 1.048.

Ratio of d to 1.85 = 1.038.

Table XIII.

Original wt. normal concentration of solution, 0.7. Experiment No. 1.
 Rotation of original solution, 35°.30. Manometer used, No. 20.
 Rotation at conclusion of experiment, 34°.95. Capillary depression, 0.02.
 Loss in concentration, 0°.35 = 0.99 per cent. Cell used, D.
 Calibration units of air in manometer, 495.09. Resistance of membrane, 364,000.
 Time of setting up cell, 4.30 P.M., Feb. 21, 1907. Initial pressure, 15.68 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.							
Feb. 21											
5.45 P.M.	0°.12	2°.00	31.07	30.84							
8.00 "	0°.10	0°.70	29.93	29.85							
Feb. 22											
12.45 A.M.	0°.10	0°.55	29.79	29.73	1.00	0.61	0.17	0.02	16.45	15.59	0.86
"	0°.06	0°.43	29.80	29.75	1.01	0.61	0.17	0.02	16.43	15.59	0.84
1.00 P.M.	0°.08	0°.43	29.79	29.74	1.01	0.61	0.17	0.02	16.44	15.59	0.85
4.00 "	0°.08	0°.49	29.77	29.72	1.01	0.61	0.17	0.02	16.45	15.59	0.86
	0°.08										

Displacement of manometer = 0.12 mm.

Results, if corrected for whole loss in rotation:

Correction = 0.17 atmosphere.

Osmotic pressure = 16.44 atmospheres.

Molecular pressure = 23.49 atmospheres.

Ratio of osmotic to gas pressure = 1.055.

Results, if corrected for half the loss in rotation:

Correction = 0.085 atmosphere.

Osmotic pressure = 16.36 atmospheres.

Molecular pressure = 23.37 atmospheres.

Ratio of osmotic to gas pressure = 1.049.

Ratio of Δ to 1.85 = 1.038.

Table XIV.

Original wt. normal concentration of solution, 0.7.
 Experiment No. 2.
 Rotation of original solution, $35^{\circ}.25$.
 Manometer used, No. 20.
 Rotation at conclusion of experiment, $35^{\circ}.05$.
 Capillary depression, 0.02.
 Loss in concentration, $0^{\circ}.20 = 0.57$ per cent.
 Cell used, D.
 Resistance of membrane, 365,000.
 Calibration units of air in manometer, 495.09.
 Initial pressure, 15.54 atmospheres.
 Time of setting up cell, 5.30 P.M., Feb. 23, 1907.

Time.	Temperature.		Volume of air in manometer.		Corrections.			Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Osmotic pressure corrected.	
Feb. 23									
6.30 P.M.	$0^{\circ}.06$	$0^{\circ}.85$	31.18	31.08					
8.15 "	$0^{\circ}.07$	$0^{\circ}.59$	29.75	29.69					
12.00 "	$0^{\circ}.06$	$0^{\circ}.51$	29.68	29.62	1.02	0.61	0.10	16.42	15.59 0.83
Feb. 24									
10.15 A.M.	$0^{\circ}.06$	$0^{\circ}.48$	29.66	29.61	1.02	0.61	0.10	16.42	15.59 0.83
	$0^{\circ}.06$								

Displacement of manometer = 0.00.

Results, if corrected for whole loss in rotation:

Correction = 0.10 atmospheres.

Osmotic pressure = 16.42 atmospheres.

Molecular pressure = 23.46 atmospheres.

Ratio of osmotic to gas pressure = 1.053.

Results, if corrected for half the loss in rotation:

Correction = 0.05 atmospheres.

Osmotic pressure = 16.37 atmospheres.

Molecular pressure = 23.39 atmospheres.

Ratio of osmotic to gas pressure = 1.050.

Ratio of λ to 1.85 = 1.038.

Table XV.

Original wt. normal concentration of solution, 0.8. Experiment No. 1.
 Rotation of original solution, $39^{\circ}85$. Manometer used, No. 20.
 Rotation at conclusion of experiment, $39^{\circ}40$. Capillary depression, 0.02.
 Loss in concentration, $0^{\circ}45 = 1.13$ per cent. Cell used, G.
 Calibration units of air in manometer, 495.09. Resistance of membrane, 550,000.
 Time of setting up cell, 3.45 P.M., Feb. 26, 1907. Initial pressure, 17.52 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.			Theoretical gas pressure found and calculated.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Osmotic pressure corrected.	
Feb. 26									
5.00 P.M.	$0^{\circ}12$	$2^{\circ}60$	27.93	27.68					
8.00 "	$0^{\circ}12$	$0^{\circ}73$	26.18	26.11					
11.00 "	$0^{\circ}12$	$0^{\circ}70$	26.15	26.08	1.00	0.62	0.22	18.84	17.82 1.02
Feb. 27									
10.00 A.M.	$0^{\circ}12$	$0^{\circ}75$	26.15	26.08	1.00	0.62	0.22	18.84	17.82 1.02
1.00 P.M.	$0^{\circ}15$	$0^{\circ}83$	26.13	26.05	1.00	0.62	0.22	18.87	17.82 1.05
4.00 "	$0^{\circ}14$	$0^{\circ}83$	26.11	26.03	1.01	0.62	0.22	18.87	17.82 1.05

$0^{\circ}13$ Displacement of manometer = 0.20 mm.

Results, if corrected for whole loss in rotation:

Correction = 0.22 atmosphere.

Osmotic pressure = 18.86 atmospheres.

Molecular pressure = 23.57 atmospheres.

Ratio of osmotic to gas pressure = 1.058.

Results, if corrected for half the loss in rotation:

Correction = 0.11 atmosphere.

Osmotic pressure = 18.75 atmospheres.

Molecular pressure = 23.43 atmospheres.

Ratio of osmotic to gas pressure = 1.052.

Ratio of 4 to 1.85 = 1.038.

Table XVI.

Original wt. normal concentration of solution, 0.8.
 Rotation of original solution, $39^{\circ} 85$.
 Rotation at conclusion of experiment, $39^{\circ} 50$.
 Loss in concentration, $0^{\circ} 35 = 0.88$ per cent.
 Calibration units of air in manometer, 478.16.
 Time of setting up cell, 4.00 P.M., Feb. 26, 1907.

Time.	Temperature.		Volume of air in manometer.		Atmospheric pressure.	Corrections.			Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.		Liquids in manometer.	Dilution of cell contents.	Capillary depression.			
Feb. 26											
5.00 P.M.	0° 12	2° 60	27.12	26.88	1.00	0.55	0.17	0.02	18.84	17.82	1.02
8.00 "	0° 12	0° 73	25.10	25.03	1.00	0.55	0.17	0.02	18.90	17.82	1.08
11.00 "	0° 12	0° 70	25.02	24.96							
Feb. 27											
10.00 A.M.	0° 12	0° 75	25.08	25.01	1.00	0.55	0.17	0.02	18.86	17.82	1.04
1.00 P.M.	0° 15	0° 83	25.10	25.02	1.00	0.55	0.17	0.02	18.85	17.82	1.03
4.00 "	0° 14	0° 83	25.09	25.01	1.01	0.55	0.17	0.02	18.85	17.82	1.03
	0° 13		Displacement of manometer = 0.05. mm.								

Results, if corrected for whole loss in rotation:
 Correction = 0.17 atmosphere.
 Osmotic pressure = 18.86 atmospheres.
 Molecular pressure = 23.58 atmospheres.
 Ratio of osmotic to gas pressure = 1.058.

Results, if corrected for half the loss in rotation:
 Correction = 0.085 atmosphere.
 Osmotic pressure = 17.78 atmospheres.
 Molecular pressure = 23.47 atmospheres.
 Ratio of osmotic to gas pressure = 1.054.
 Ratio of λ to 1.85 = 1.038.

Table XVII.

Original wt. normal concentration of solution, 0.9.
 Rotation of original solution, $44^{\circ}.40$.
 Rotation at conclusion of experiment, $43^{\circ}.70$.
 Loss in concentration, $0^{\circ}.70 = 1.58$ per cent.
 Calibration units of air in manometer, 495.09.
 Time of setting up cell, 3.45 P.M., March 1, 1907.

Experiment No. 1.
 Manometer used, No. 20.
 Capillary depression, 0.02.
 Cell used, G.

Resistance of membrane, 560,000.
 Initial pressure, 19.55 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.			Osmotic pressure corrected.	Difference between theoretical gas pressure pres- found and sure. calculated.
	Solution.	Air in manometer.	Uncor- rected.	Corrected.	Atmos- pheric pres- sure.	Liquids in manom- eter.	Dilu- tion of cell con- tents.		
March 1									
5.00 P.M.	$0^{\circ}.12$	$3^{\circ}.50$	25.19	24.87					
7.30 "	$0^{\circ}.12$	$0^{\circ}.78$	23.28	23.21					
11.00 "	$0^{\circ}.10$	$0^{\circ}.73$	23.24	23.18	1.00	0.62	0.35	21.35	20.05
March 2									
10.30 A.M.	$0^{\circ}.14$	$0^{\circ}.86$	23.25	23.18	0.99	0.62	0.35	21.36	20.05
12.45 P.M.	$0^{\circ}.16$	$1^{\circ}.05$	23.26	23.17	0.99	0.62	0.35	21.37	20.05
5.00 "	$0^{\circ}.24$	$1^{\circ}.10$	23.25	23.16	0.99	0.62	0.35	21.38	20.05
	$0^{\circ}.16$								

Displacement of manometer = 0.15 mm.

Results, if corrected for whole loss in rotation:

Correction = 0.35 atmosphere.

Osmotic pressure = 21.37 atmospheres.

Molecular pressure = 23.74 atmospheres.

Ratio of osmotic to gas pressure = 1.066 .

Results, if corrected for half the loss in rotation:

Correction = 0.175 atmosphere.

Osmotic pressure = 21.19 atmospheres.

Molecular pressure = 23.54 atmospheres.

Ratio of osmotic to gas pressure = 1.057 .

Ratio of d to $1.85 = 1.038$.

Table XVIII.

Original wt. normal concentration of solution, 0.9.
 Rotation of original solution, $44^{\circ}.40$.
 Rotation at conclusion of experiment, $44^{\circ}.00$.
 Loss in concentration, $0^{\circ}.40 = 0.91$ per cent.
 Calibration units of air in manometer, 478.16.
 Time of setting up cell, 4.00 P.M. March 1, 1907.

Time.	Temperature.		Volume of air in manometer.		Atmospheric pressure.	Liquids in manometer.	Dilution of cell contents.	Capillary depression.	Osmotic pressure corrected.	Difference between theoretical gas pressure and pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.						
March 1										
5.00 P.M.	$0^{\circ}.12$	$3^{\circ}.50$	23.98	23.68						
7.30 "	$0^{\circ}.12$	$0^{\circ}.78$	22.20	22.14	1.00	0.56	0.20	0.02	21.38	20.05 1.33
11.00 "	$0^{\circ}.10$	$0^{\circ}.73$	22.14	22.08	1.00	0.56	0.20	0.02	21.44	20.05 1.39
March 2										
10.45 A.M.	$0^{\circ}.14$	$0^{\circ}.86$	22.18	22.11	0.99	0.56	0.20	0.02	21.41	20.05 1.36
12.45 P.M.	$0^{\circ}.16$	$1^{\circ}.05$	22.24	22.15	0.99	0.56	0.20	0.02	21.38	20.05 1.33
5.00 "	$0^{\circ}.24$	$1^{\circ}.10$	22.24	22.15	0.99	0.56	0.20	0.02	21.38	20.05 1.33

Displacement of manometer = 0.02 mm.

Results, if corrected for whole loss in rotation:
 Correction = 0.20 atmosphere.

Osmotic pressure = 21.40 atmospheres.
 Molecular pressure = 23.78 atmospheres.
 Ratio of osmotic to gas pressure = 1.067.

Results, if corrected for half the loss in rotation:
 Correction = 0.10 atmosphere.

Osmotic pressure = 21.30 atmospheres.
 Molecular pressure = 23.66 atmospheres.
 Ratio of osmotic to gas pressure = 1.062.
 Ratio of 4 to 1.85 = 1.038.

Table XIX.

Original wt. normal concentration of solution, 1.0. Experiment No. 1.
 Rotation of original solution, $48^{\circ}.90$. Manometer used, No. 20.
 Rotation at conclusion of experiment, $48^{\circ}.20$. Capillary depression, 0.02.
 Loss in concentration, $0^{\circ}.70 = 1.43$ per cent. Cell used, D.
 Calibration units of air in manometer, 495.09. Resistance of membrane, 540,000.
 Time of setting up cell, 3.35 P.M., March 4, 1907. Initial pressure, 22.33 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.			Difference Theoret- ical gas pres- sure found and calculated.
	Solution.	Air in manom- eter.	Uncor- rected.	Corrected.	Atmos- pheric pres- sure.	Liquids in manom- eter.	Dilu- tion of cell con- tent.	Osmotic pres- sure cor- rected.
March 4								
6.00 P.M.	$0^{\circ}.17$	$2^{\circ}.40$	22.01	21.82				
11.00 "	$0^{\circ}.12$	$0^{\circ}.74$	20.87	20.82	1.00	0.62	0.34	23.76
March 5								
8.50 A.M.	$0^{\circ}.16$	$0^{\circ}.73$	20.87	20.82	1.00	0.62	0.34	23.76
12.45 P.M.	$0^{\circ}.18$	$0^{\circ}.90$	20.88	20.81	1.00	0.62	0.34	23.77
4.15 "	$0^{\circ}.22$	$1^{\circ}.07$	20.90	20.82	0.99	0.62	0.34	23.77
	$0^{\circ}.17$							22.27
								22.28
								22.28
								22.28
								22.28

Displacement of manometer = 0.15 mm.

Results, if corrected for whole loss in rotation:
 Correction = 0.34 atmosphere.

Osmotic pressure = 23.77 atmospheres.

Molecular pressure = 23.77 atmospheres.

Ratio of osmotic to gas pressure = 1.067.

Results, if corrected for half the loss in rotation:
 Correction = 0.17 atmosphere.

Osmotic pressure = 23.60 atmospheres.

Molecular pressure = 23.60 atmospheres.

Ratio of osmotic to gas pressure = 1.059.

Ratio of d to $1.85 = 1.038$.

Table XX.

Original wt. normal concentration of solution, 1.0.
 Rotation of original solution, $48^{\circ}.90$.
 Rotation at conclusion of experiment, $48^{\circ}.32$.
 Loss in concentration, $0^{\circ}.58 = 1.20$ per cent.
 Calibration units of air in manometer, 478.16.
 Time of setting up cell, 4.15 P.M., March 4, 1907.

Experiment No. 2.
 Manometer used, No. 21.
 Capillary depression, 0.02.
 Cell used, G.
 Resistance of membrane, 540,000.
 Initial pressure, 22.95 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.			Difference between theoretical gas pressure pres- found and calculated.
	Solution.	Air in manometer.	Uncor- rected.	Corrected.	Atmos- pheric pres- sure.	Liquids in manometer.	Dilu- tion of cell contents.	Osmotic pres- sure cor- rected.
March 4								
6.00 P.M.	$0^{\circ}.17$	$2^{\circ}.40$	20.64	20.46				
11.30 "	$0^{\circ}.12$	$0^{\circ}.74$	20.06	20.01	1.00	0.56	0.30	0.02
March 5								
10.00 A.M.	$0^{\circ}.16$	$0^{\circ}.85$	20.11	20.05	1.00	0.56	0.30	0.02
12.45 P.M.	$0^{\circ}.18$	$0^{\circ}.90$	20.18	20.11	1.00	0.56	0.30	0.02
4.15 "	$0^{\circ}.22$	$1^{\circ}.07$	20.17	20.09	0.99	0.56	0.30	0.02
	$0^{\circ}.17$							

Displacement of manometer = 0.09 mm.

Results, if corrected for whole loss in rotation:
 Correction = 0.30 atmosphere.
 Osmotic pressure = 23.72 atmospheres.
 Molecular pressure = 23.72 atmospheres.
 Ratio of osmotic to gas pressure = 1.064.

Results, if corrected for half the loss in rotation:
 Correction = 0.15 atmosphere.
 Osmotic pressure = 23.57 atmospheres.
 Molecular pressure = 23.57 atmospheres.
 Ratio of osmotic to gas pressure = 1.055.
 Ratio of Δ to 1.85 = 1.038.

Table XXII.—Results for Each Experiment, if Correction Is Made for the Whole Loss in Rotation.

Weight normal concen- tration.	No. of experi- ment.	Tem- perature.	Correc- tion. Atmos- pheres.	Osmotic pressure. Atmos- pheres.	Calculated gas pressure. Atmos- pheres.	Molecular osmotic pressure. Atmos- pheres.	Molecular gas pressure. Atmos- pheres.	Ratio of osmotic to gas pressure.
1	2	3	4	5	6	7	8	9
0.1	1	0°.28	0.01	2.40	2.23	23.95	22.28	1.074
"	2	0°.24	0.00	2.40	2.23	24.03	"	1.077
0.2	1	0°.12	0.05	4.66	4.45	23.29	"	1.047
"	2	0°.13	0.03	4.68	4.45	23.39	"	1.051
0.3	1	0°.19	0.05	7.04	6.68	23.45	"	1.054
"	2	0°.22	0.06	7.04	6.68	23.48	"	1.054
0.4	1	0°.12	0.08	9.35	8.91	23.37	"	1.049
"	2	0°.21	0.09	9.33	8.91	23.33	"	1.047
0.5	1	0°.17	0.07	11.69	11.14	23.39	"	1.050
"	2	0°.24	0.12	11.69	11.14	23.38	"	1.049
0.6	1	0°.12	0.22	14.12	13.36	23.53	"	1.057
"	2	0°.08	0.22	14.12	13.36	23.53	"	1.057
0.7	1	0°.08	0.17	16.44	15.59	23.49	"	1.055
"	2	0°.06	0.10	16.42	15.59	23.46	"	1.053
0.8	1	0°.13	0.22	18.86	17.82	23.57	"	1.058
"	2	0°.13	0.17	18.86	17.82	23.58	"	1.058
0.9	1	0°.16	0.35	21.37	20.05	23.74	"	1.066
"	2	0°.15	0.20	21.40	20.05	23.78	"	1.067
1.0	1	0°.17	0.34	23.77	22.28	23.77	"	1.067
"	2	0°.17	0.30	23.72	22.28	23.72	"	1.064

Mean ratio = 1.058

Table XXIII.—Results for Each Concentration, if Correction Is Made for the Whole Loss in Rotation

Weight normal concentration.	Tem- perature.	Osmotic pressure. Atmos- pheres.	Calculated gas pressure. Atmos- pheres.	Molecular osmotic pressure. Atmos- pheres.	Molecular gas pressure. Atmos- pheres.	Ratio of osmotic to gas pressure.
1	2	3	4	5	6	7
0.1	0°.26	2.40	2.23	23.99	22.28	1.076
0.2	0°.13	4.67	4.45	23.34	"	1.049
0.3	0°.21	7.04	6.68	23.47	"	1.054
0.4	0°.17	9.34	8.91	23.35	"	1.048
0.5	0°.21	11.69	11.14	23.39	"	1.050
0.6	0°.10	14.12	13.36	23.53	"	1.057
0.7	0°.07	16.43	15.59	23.48	"	1.054
0.8	0°.13	18.86	17.82	23.58	"	1.058
0.9	0°.16	21.39	20.05	23.76	"	1.067
1.0	0°.17	23.75	22.28	23.75	"	1.066

Mean ratio = 1.058

Table XXIV.—Results for Each Experiment, if Correction Is Made for Half the Loss in Rotation.

Weight normal con- centration.	No. of experi- ment.	Tem- pera- ture.	Correction. Atmos- pheres.	Osmotic pressure. Atmos- pheres.	Calculated gas pressure. Atmos- pheres.	Molecular osmotic pressure. Atmos- pheres.	Molecular gas pressure. Atmos- pheres.	Ratio of osmotic to gas pressure.	Ratio of Δ to 1.85.
1	2	3	4	5	6	7	8	9	10
0.1	1	0°.28	0.005	2.39	2.23	23.90	22.28	1.072	1.038
"	2	0°.24	0.000	2.40	2.23	24.03	"	1.077	"
0.2	1	0°.12	0.025	4.63	4.45	23.16	"	1.041	"
"	2	0°.13	0.015	4.66	4.45	23.31	"	1.048	"
0.3	1	0°.19	0.025	7.01	6.68	23.38	"	1.050	"
"	2	0°.22	0.030	7.01	6.68	23.37	"	1.049	"
0.4	1	0°.12	0.040	9.31	8.91	23.27	"	1.045	"
"	2	0°.21	0.045	9.29	8.91	23.21	"	1.042	"
0.5	1	0°.17	0.035	11.66	11.14	23.32	"	1.047	"
"	2	0°.24	0.060	11.63	11.14	23.26	"	1.044	"
0.6	1	0°.12	0.110	14.01	13.36	23.34	"	1.048	"
"	2	0°.08	0.110	14.01	13.36	23.34	"	1.048	"
0.7	1	0°.06	0.085	16.37	15.59	23.37	"	1.049	"
"	2	0°.06	0.050	16.37	15.59	23.39	"	1.050	"
0.8	1	0°.13	0.110	18.75	17.82	23.43	"	1.052	"
"	2	0°.13	0.085	18.78	17.82	23.47	"	1.054	"
0.9	1	0°.16	0.175	21.19	20.05	23.54	"	1.057	"
"	2	0°.15	0.100	21.30	20.05	23.66	"	1.062	"
1.0	1	0°.17	0.170	23.60	22.28	23.60	"	1.059	"
"	2	0°.17	0.150	23.57	22.28	23.57	"	1.055	"

Ratio of Δ to 1.84 = 1.043

Mean ratio = 1.053

Table XXV.—Results for Each Concentration, if Correction Is Made for Half the Loss in Rotation.

Weight normal con- cen- tra- tion.	Tem- pera- ture.	Osmotic pressure. Atmos- pheres.	Calculated gas pressure. Atmos- pheres.	Molecular osmotic pressure. Atmos- pheres.	Molecular gas pressure. Atmos- pheres.	Ratio of osmotic to gas pressure.	Ratio of Δ to 1.85.
1	2	3	4	5	6	7	8
0.1	0°.26	2.40	2.23	23.97	22.28	1.075	1.038
0.2	0°.13	4.65	4.45	23.24	"	1.045	"
0.3	0°.21	7.01	6.68	23.38	"	1.050	"
0.4	0°.17	9.30	8.91	23.24	"	1.044	"
0.5	0°.21	11.65	11.14	23.29	"	1.046	"
0.6	0°.10	14.01	13.36	23.34	"	1.048	"
0.7	0°.07	16.37	15.59	23.38	"	1.050	"
0.8	0°.13	18.77	17.82	23.45	"	1.053	"
0.9	0°.16	21.25	20.05	23.60	"	1.060	"
1.0	0°.17	23.59	22.28	23.59	"	1.057	"

Ratio of Δ to 1.84 = 1.043

Mean ratio = 1.053

provement over former measurements is important as eliminating a source of dilution. The loss in rotation is given both in degrees and in percentage. Column 8 contains the equivalent of the loss in rotation in atmospheres. These values were used in correcting the observed pressures for dilution.

Table XXII. gives the results for each experiment when correction is made for the whole loss in rotation. The values given are the means of the several observations made during each experiment. For the calculation of the theoretical gas pressure at the temperature of the experiment, the weight of 1 liter of hydrogen, under standard conditions, was taken as 0.089826 gram (Morley's value), and the molecular weight of hydrogen as 2. A gram-molecular weight of hydrogen, reduced to a volume of 1 liter at 0°, exerts a pressure of 22.265 atmospheres. The pressure at the temperature of the experiment is calculated by the formula

$$P = 22.265 (1 + 0.00367 t).$$

The molecular osmotic pressures were obtained by dividing the observed pressures by the normality of the solution.

*Table XXVI.—Results for Each Concentration, if Correction Is Made for Half the Loss in Rotation.
Cane Sugar. Series III.*

1	2	3	4	5	6	7	8	9	10
Weight normal con- centration.	Tem- perature.	Osmotic pressure, Atmos- pheres.	Calculated gas pressure, Atmos- pheres.	Molecular osmotic pressure, Atmos- pheres.	Molecular gas pressure, Atmos- pheres.	Molecular depres- sion of the freezing point.	Ratio of Δ to 1.84.	Ratio of Δ to 1.85.	Ratio of osmotic to gas pressure.
0.1	0°.24	2.44	2.23	24.40	22.29	1°.95	1.060	1.054	1.094
0.2	0°.26	4.80	4.46	24.00	"	1°.96	1.065	1.059	1.076
0.3	0°.22	7.16	6.69	23.87	"	1°.95	1.060	1.054	1.071
0.4	0°.24	9.40	8.92	23.50	"	1°.96	1.065	1.059	1.054
0.5	0°.19	11.85	11.14	23.70	"	1°.97	1.071	1.065	1.064
0.6	0°.22	14.25	13.37	23.75	"	1°.98	1.076	1.070	1.066
0.7	0°.23	16.81	15.60	24.01	"	1°.99	1.081	1.076	1.078
0.8	0°.23	19.33	17.83	24.16	"	2°.02	1.098	1.092	1.084
0.9	0°.27	22.13	20.06	24.59	"	2°.03	1.103	1.097	1.103
1.0	0°.25	24.78	22.28	24.78	"	2°.07	1.125	1.119	1.112

The results in Table XXII. are given in a more compact form in Table XXIII., the mean values for each concentration being given.

Table XXIV. gives the results for each experiment and Table XXV. for each concentration, when only one-half the loss in rotation is used to correct for dilution. The reason for making the correction on this basis was discussed under the head of dilution. The results obtained in this manner are considered to be more nearly the true values than those obtained by correcting for the whole loss in rotation.

Table XXVI. is added for the sake of comparing the results obtained with cane-sugar solutions¹ at about 0° with those of glucose solutions at the same temperature.

Discussion of Results.

An inspection of Table XXV., columns 3 and 4, shows that the observed osmotic pressures are higher than the gas pressures calculated for the same temperature, and that the difference increases with the concentration. In fact, the difference is proportional to the concentration, since the molecular osmotic pressure is practically a constant.

The molecular osmotic pressure for the 0.1 normal solution is considerably higher than for the other concentrations. This is undoubtedly due to the fact that the sum of all experimental errors, especially the error due to the osmotic inequality of the "membrane-formers," has more effect on the small pressure of this solution than on the pressures of solutions of higher concentration. However, the molecular pressure appears to be constant, within the limits of unavoidable experimental error. To what extent this is true, is better shown by the ratio of osmotic to gas pressure, column 7. The highest value here is 1.075 for the 0.1 normal concentration, and the lowest, 1.044 for the 0.4 normal, the mean being 1.053. With the exception of the 0.1 normal, the maximum variation is 1.6 percent, and the greatest difference from the mean is 0.9 percent. The values from the 0.2 normal to the 0.8 normal, inclusive, are in close agreement with the mean. It appears, then, that the

¹ Am. Chem. J., 37, 425.

osmotic pressure of glucose solutions near 0° is directly proportional to the concentration.

This result apparently shows that glucose exists in solution in the anhydrous condition. Since all the solutions were made up with a constant amount of water, the direct proportionality between pressure and concentration shows that the glucose can not have appropriated any of the solvent. For, if the abnormally high pressures are explained on the basis of hydration, we are led to the conclusion that the same absolute amount of water is abstracted in every solution, irrespective of the concentration. This conclusion, that glucose is anhydrous in solution, is also in agreement with the freezing point lowering of glucose solutions¹ (weight-normal solutions). A constant molecular lowering of the freezing point is obtained, showing that the depression of the freezing point is strictly proportional to the concentration.

It may appear, from the fact that osmotic pressures in the vicinity of 0° are considerably in excess of the calculated gas pressures and approach very nearly to the pressures obtained at 20° , that osmotic pressure has little or no temperature coefficient. It is not thought that sufficient experimental data is at hand to justify any conclusion on this point. Since the osmotic pressures found at the higher temperatures (18° to 26°) agree well with the calculated gas pressures, it is probable that at some intermediate temperature a minimum pressure will be found and that the pressure will increase in both directions from this point. For this reason experiments have been begun at different temperatures between 0° and 20° .²

As is well known, both the freezing point lowering and the osmotic pressure of solutions are dependent on the number of dissolved particles relative to a given mass of solvent. Hence, knowing the freezing point of a solution, it is possible to calculate its osmotic pressure. It might be expected that the observed osmotic pressure of glucose solutions near 0° would agree with the pressure calculated from the freezing point lowering. How well these two sets of values do agree is shown in Table XXVII. The calculated pressures were obtained by the formula,

$$\frac{G. P.}{1.85} \times \Delta \times (1 + 0.00367 t) = \text{osmotic pressure,}$$

¹ *Am. Chem. J.*, **37**, 360.

² P. B. Dunbar, Dissertation, Johns Hopkins University (1907).

in which G. P. is the molecular gas pressure at the freezing point

Table XXVII.

Weight-normal concentration. 1	Osmotic pressure calculated from the freez- ing point lowering. 2	Observed osmotic pressure. 3	Difference. 4
0.1	2.31	2.40	0.09
0.2	4.62	4.65	0.03
0.3	6.93	7.01	0.08
0.4	9.24	9.30	0.06
0.5	11.56	11.65	0.09
0.6	13.87	14.01	0.14
0.7	16.18	16.37	0.19
0.8	18.50	18.77	0.27
0.9	20.80	21.25	0.45
1.0	23.11	23.59	0.48

of the solution, 1.85, the calculated molecular lowering of the freezing point and Δ , the observed freezing point depression. The factor $(1 + 0.00367 t)$ brings the pressure from the freezing point of the solution to the temperature at which the osmotic pressure was measured. The ratio of osmotic to gas pressure should also agree approximately with the ratio of the observed molecular lowering of the freezing point to 1.85. This is shown in Table XXV., columns 7 and 8.

Other relations might be brought out connecting the osmotic pressures of solutions of cane-sugar and of glucose with their freezing point depressions. Thus, if we represent by

P, the osmotic pressure of glucose.

P₁, " " cane-sugar.

Δ , the observed molecular depression of the freezing point of glucose.

Δ_1 , the observed molecular depression of the freezing point of cane-sugar.

R, the ratio of osmotic to gas pressure for glucose.

R₁, " " " cane-sugar.

then proportions, such as the following, should be found to hold approximately.

$$(1) \quad P : P_1 :: \Delta : \Delta_1$$

$$(2) \quad R : R_1 :: \Delta : \Delta_1$$

$$(3) \quad R : R_1 :: \frac{\Delta}{1.85} : \frac{\Delta_1}{1.85} ; \text{etc.}$$

Exact agreement should not be expected since the temperatures, at which the osmotic pressures and freezing points are determined, are slightly different, and the differences in agreement should increase with the concentration. What agreement is found for the proportion, $P : P :: \Delta : \Delta$ (and consequently for all other proper methods of comparison) is shown in Table XXVIII. From this proportion, it appears that the osmotic pressures of glucose and of cane-sugar solutions in the neighborhood of 0° differ from the calculated gas pressures to about the same extent that their observed molecular depressions of the freezing point differ from the calculated molecular depression, 1.85.

Table XXVIII.

Weight normal con- centration.	P , osmotic pressure of glucose.	P_1 , osmotic pressure of cane sugar.	Δ observed molecular depression of the freezing point of glucose.	Δ_1 , molecu- lar depression of the freezing point of cane sugar.	
				Calcu- lated.	Observed.
0.1	2.40	2.44	1.92	1.95	1.95
0.2	4.65	4.80	"	1.98	1.96
0.3	7.01	7.16	"	1.96	1.95
0.4	9.30	9.40	"	1.94	1.96
0.5	11.65	11.85	"	1.95	1.97
0.6	14.01	14.25	"	1.95	1.98
0.7	16.37	16.81	"	1.97	1.99
0.8	18.77	19.33	"	1.98	2.02
0.9	21.25	22.13	"	2.00	2.03
1.0	23.59	24.78	"	2.02	2.07

Conclusions.

The results of this investigation show:

That the osmotic pressures of glucose solutions, like those of cane-sugar, in the vicinity of 0° are higher than the gas pressures calculated for the same temperature.

That the osmotic pressure of glucose solutions at this temperature is directly proportional to the concentration.

This proportionality between osmotic pressure and concentration seems to indicate that glucose exists in solution, even in the neighborhood of 0° , in the anhydrous condition, and that the excess of the observed molecular depressions of the freezing point (1.92) above 1.85 is not due to hydration.

II.—THE USE OF WEIGHT-NORMAL SOLUTIONS IN THE MEASUREMENT OF OSMOTIC PRESSURE.

Ostwald in his book, "Solutions," makes this statement regarding osmotic pressure: "*Dissolved substances exert the same pressure, in the form of osmotic pressure, as they would exert were they gasified, at the same temperature without change of volume.*"¹ In other words, the osmotic pressure, which is exerted by a substance in solution, is equal to the gas pressure, which it would exert, if it were gasified at the same temperature and its volume equal to that of the *solution*. This appears to be a fair statement of the view, which has been generally held, regarding the connection between osmotic pressure and gas pressure. In fact, van't Hoff himself in his paper, "The Rôle of Osmotic Pressure in the Analogy between Solutions and Gases," says: "*The directly determined osmotic pressure of a cane-sugar solution is accordingly exactly equal, at the same temperature, to the pressure of a gas which contains the same number of molecules as there are sugar molecules present in the same volume of the solution.*"²

As a later expression of the view held concerning the relation of osmotic to gas pressure, the following quotation from Nernst's "Theoretische Chemie" is given: "*The osmotic pressure of cane-sugar in solution is exactly the same as the gas pressure which would be observed if the solvent were removed, and the dissolved substance were left filling the same space in the form of a gas at the same temperature.*"³

In his paper, van't Hoff treats only of dilute solutions, and throughout his whole discussion specifies particularly dilute solutions ("verdünnte Lösungen"), having explained what he means by such an expression. In the first part of the paper, after calling attention to the possibility of applying a reversible process to solutions by the use of osmotic pressure, he states:

¹ Solutions, p. 116 (translation by Muir).

² Zeit. phys. Chem., I, 493.

³ Theoretische Chemie, p. 148, 2nd Auf. (1898).

"Practical application will be made of this in the following, especially for the investigation of the laws which hold for 'ideal solutions,' that is, for solutions, which are so dilute, that they are to be compared with 'ideal gases,' and in which the mutual action of the molecules of the dissolved substance is to be neglected, as well as the space occupied by these molecules in comparison with the volume of the solution itself."¹

Whether he meant to imply that the analogy between osmotic pressure and gas pressure would hold only for "ideal solutions," he, at least, apparently foresaw the possibility of discrepancies occurring in the case of concentrated solutions. In the above quotation, he mentions the two factors that would be likely to have disturbing influences, namely, the mutual attraction between the molecules of the dissolved substance and the space occupied by these.

Indeed, if the complete analogy between solutions and gases is accepted, it would be expected that abnormal results would be obtained in concentrated solutions; for, gases in a concentrated condition, that is, under high pressure, do not obey Boyle's law ($p v = \text{constant}$), but the product, $p v$, increases with the pressure. This deviation from Boyle's law, in the case of gases, finds an explanation in van der Waals' equation,

$$(p + a/v^2)(v - b) = \text{constant}.$$

This equation has been found to give good results, even to considerable pressures. It is probable, then, that abnormal results in concentrated solutions might be explained in a similar manner.

Ostwald² appears to be the first to have suggested the necessity of applying van der Waals' equation to solutions. In the course of a study of the electrical conductivity of solutions of a number of organic compounds, he found that the constant

in his dilution law, $\frac{m^3}{(I - m)v} = K$, decreased with the con-

centration in the case of concentrated solutions. He thought that this irregular result might be corrected by the use of van der Waals' equation. Neglecting the intramolecular attraction

¹ Zeit. phys. Chem., **1**, 483.

² Ibid., **2**, 280.

of the molecules of the dissolved substance, he introduced factors for the space occupied by the dissolved substance and, also, for the inner friction of the solution. With the new equation, thus obtained, he found a satisfactory constant.

Arrhenius¹ and Beckmann² suggested, as an explanation of certain abnormal results which they obtained in measurements of the freezing point lowering of solutions, the attraction between the molecules of the dissolved substance and, also, between these and the molecules of the solvent. However, they made no attempt to apply any correction for these attractions. Bredig,³ in a discussion on the kinetic nature of osmotic pressure, by assuming a specific attraction between the molecules of the dissolved substance and the molecules of the solvent and, also, an attraction between the molecules of the dissolved substance themselves, obtained an equation similar to that of van der Waals. By the use of this equation, he showed how the properties of concentrated solutions, in respect to their freezing point depressions, could be explained.

A. A. Noyes⁴ has shown how van der Waals' equation may be applied to osmotic pressure. In applying this equation to solutions, Noyes disregards the attraction between the molecules of the dissolved substance, which is small in comparison with the pressure, and considers only the volumes of the molecules of the dissolved substance and of the solvent, and the attraction between the molecules of the solvent and those of the dissolved substance. The latter attraction, he says, may or may not exist and that the same result is obtained whether it is regarded or not.

After introducing these factors, his equation reduces finally to the form,

$$p(v - d) = K,$$

in which p is the osmotic pressure, v the volume of the solution which contains a gram-molecular weight of the dissolved substance, d a constant which depends on the volumes of the molecules of the dissolved substance and of the solvent and the

¹ Zeit. phys. Chem., **2**, 499.

² *Ibid.*, **2**, 734.

³ *Ibid.*, **4**, 444.

⁴ *Ibid.*, **5**, 53.

attraction between these, and K a constant which is the molecular osmotic pressure. The value of d is determined experimentally from two sets of measurements. Thus, if p and v are the pressure and volume, respectively, in one case and if p_2 and v_2 have the same significance in another, then,

$$p_1(v_1 - d) = p_2(v_2 - d)$$

and

$$d = \frac{p_2 v_2 - p_1 v_1}{p_2 - p_1}.$$

Noyes applied this equation to certain irregular freezing point lowerings, when he obtained a constant value for the molecular depression of the freezing point.

Thos. Ewan¹ applied van der Waals' equation to solutions in obtaining a theoretical relation between osmotic pressure and concentration. If the heat of dilution is zero, his equation assumes the form,

$$p(v - b) = RT,$$

which, for very dilute solutions, becomes Boyle's law,

$$pv = RT.$$

In a later paper² on the osmotic pressure of concentrated solutions, he made use of an equation of the same general form as that of van der Waals for calculating osmotic pressure. He compared the osmotic pressures, thus obtained, with those calculated from the freezing point depression.

Abegg,³ in the theoretical portion of a paper on the freezing point lowerings of concentrated solutions, discussed the application of van der Waals' equation to solutions.

Among others who have made use of van der Waals' equation in the study of solutions may be mentioned Schilling,⁴ Barmwater⁵ and Loomis.⁶

In the preliminary work, in this laboratory, on the osmotic pressure of cane-sugar solutions, it at once became apparent that osmotic pressure does not strictly obey the gas laws according to the original formulation of van't Hoff. While this

¹ Zeit. phys. Chem., **14**, 417.

² Ibid., **31**, 22.

³ Ibid., **15**, 254.

⁴ Progr. d. Oberrealschule in Olmütz, 1893/4, 23.

⁵ Zeit. phys. Chem., **28**, 115.

⁶ Ibid., **37**, 407.

relation between osmotic pressure and gas pressure holds for dilute solutions, it does not for concentrated solutions. In the case of cane-sugar solutions, marked discrepancies were found. The osmotic pressure of the normal solution (*i. e.*, volume-normal) was found to be just about 31.5 atmospheres at 24° while the calculated gas pressure at this temperature is only 24.25 atmospheres. Instead of obeying Boyle's law, $p v = K$, it was found that the product, $p v$, increases rapidly with the concentration.

Accepting the analogy between gas pressure and osmotic pressure, it was suspected that the abnormalities in the latter could be accounted for in the same way as in the case of gases, and correction made by an application of van der Waals' equation. Of the two factors introduced into Boyle's law by van der Waals, the one for the intramolecular attraction is probably so small in comparison with the pressure that it can be neglected. As in the case of gases, the true volume is not the total space occupied by the gas, but this diminished by the volume of the molecules of the gas, so in solutions, it is probable that the true volume is not that of the solution, but this diminished by the volume of the molecules of the dissolved substance, that is, the volume of the solvent.

If this be true, it was thought that correction could be made for the space occupied by the molecules of the dissolved substance by preparing the solutions with a fixed mass of water. For this reason the change from the volume-normal to the weight-normal basis was made.

When this was done, osmotic pressures were obtained that are strictly proportional to the concentration. This led to the conclusion that, "*Cane-sugar dissolved in water exerts an osmotic pressure equal to that which it would exert if it were gasified at the same temperature and the volume of the gas were reduced to that of the solvent in the pure state.*"¹ This rule has also been found to hold for glucose solutions.²

It should be stated that while this rule holds at the temperatures at which measurements were first made (between 18°

¹ Am. Chem. J., **34**, 93; **36**, 87.

² Ibid., **37**, 357.

and 26° in round numbers), it does not at temperatures in the neighborhood of 0° ,¹ abnormally high pressures being obtained. The osmotic pressures of cane-sugar solutions near 4° ² are also higher than the theoretical gas pressures for the same temperature. Although the pressures obtained at these low temperatures are higher than the calculated gas pressures, still they are directly proportional (for glucose) to the concentration, that is, the osmotic pressure obeys Boyle's law. While the pressures obtained with cane-sugar solutions at low temperatures are not strictly proportional to the concentration in the more concentrated solutions, they vary to about the same extent as the observed molecular depressions of the freezing point (see Table XXVI.).

Since the pressures obtained by preparing the solutions with a fixed amount of water are directly proportional to the concentration (both cane-sugar and glucose at 18° to 26° and glucose at 0°), it appears that in this way correction is made for the space occupied by the molecules of the dissolved substance. The standard volume, then, for osmotic pressure must be regarded not as the volume of the *solution*, but as that of the *solvent*. The volume of the solvent in solutions, therefore, is the analogue of that volume in gases, which is equal to the total space occupied by the gas diminished by the volume of the gas molecules.

According to the rule given above for the relation of osmotic to gas pressure, this volume is assumed to be that of the solvent in the pure state. If varying amounts of substance are dissolved in a fixed amount of water, the volume of the water in the pure state will be the standard volume, provided there are no volume changes when the solutions are made up, that is, provided the volume of the solution is equal to the volume of the water plus the volume of the dissolved substance.

With the view of throwing some light on this question, the densities of the solutions of cane-sugar and also of glucose were determined.³ The densities of cane-sugar solutions were measured at different temperatures. This question of volume

¹ Am. Chem. J., **37**, 465. See also this Dissertation, Table XXV.

² P. B. Dunbar, Dissertation, Johns Hopkins University (1907).

³ Am. Chem. J., **34**, 97; **36**, 91; **37**, 360.

changes has been studied more closely in the case of glucose solutions at 0° .

In order to know the volume of a given weight of glucose, it is, of course, necessary to know its density. As no value for the density of glucose at 0° could be found in the literature, this was determined as follows:

The method employed was the displacement of strong alcohol, which had been saturated at 0° with glucose, the density of this solution having been previously determined. A bottle pycnometer of 50 cc. capacity was used. A glass tube with a bulb on it was ground to fit the capillary tube on the pycnometer and was put on after the pycnometer had been filled, in order to hold the alcohol that overflowed when it warmed up to the temperature of the room. A weighed amount of glucose was put into the pycnometer, which was then filled with the saturated alcohol while it was immersed in an ice bath. The combined weight of the glucose and the alcohol was then determined. If W = the weight of the alcohol that fills the pycnometer at 0° ,

d_1 = the density of the alcohol at 0° ,

w_1 = the weight of the glucose,

w_2 = the weight of the glucose and alcohol required to fill the pycnometer,

d = the density of the glucose,

then

$$d = \frac{w_1 \times d_1}{w - (w_2 - w_1)}.$$

The weighings were made against another pycnometer of the same size by the method of substitution and all the weights were corrected for air displacement.

Three determinations of the density gave the results,

1.5572

1.5566

1.5563

Mean = 1.5567

The mean value, 1.5567, was employed in calculating the volumes of the different weights of glucose used in making the solutions.

Table XXIX.

Weight-normal concentration.	Volume of the water, cc.	Volume of the glucose, cc.	Sum of the volumes of water and glucose, cc.	Volume ¹ of the solution, cc.	Difference.	
1	2	3	4	5	6	7
0.1	1000.13	11.48	1011.61	1010.93	0.68	0.07
0.2	"	22.96	1023.09	1021.70	1.39	0.14
0.3	"	34.45	1034.58	1032.55	2.03	0.20
0.4	"	45.93	1046.06	1043.42	2.64	0.25
0.5	"	57.41	1057.54	1054.29	3.25	0.31
0.6	"	68.89	1069.02	1065.22	3.80	0.36
0.7	"	80.37	1080.50	1076.14	4.36	0.40
0.8	"	91.86	1091.99	1087.06	4.93	0.45
0.9	"	103.34	1103.47	1097.94	5.53	0.50
1.0	"	114.82	1114.95	1108.92	6.03	0.54

Table XXIX. gives a comparison of the volume of the solution with the sum of the volumes of the water and of the glucose. In columns 6 and 7 is given the difference between this sum and the volume of the solution, both as the actual difference in cubic centimeters and as percentage difference. It will be seen that a slight decrease in volume occurs when glucose is dissolved in water and that the decrease is proportional to the concentration. However, the decrease is small, amounting to only 0.54 percent in the normal solution. This change probably would not produce an effect on the osmotic pressure that could be detected at the present state of refinement in the method which is now used.

The fact that the volume of the solution is practically equal to the sum of the volumes of the water and of the glucose, indicates that the true volume for osmotic pressure can be regarded as the volume of the solvent in the pure state. This justifies the assumption originally made, that by preparing the solutions on the weight-normal basis correction is automatically applied for the space occupied by the molecules of the dissolved substance.

Another line of evidence can be brought to bear upon this question. If van der Waals' equation is applied to osmotic pressure and, by the use of it, the pressures obtained on the volume-normal basis are corrected, and if these corrected pressures are equal to the pressures obtained on the weight-normal

¹ B. Smith Hopkins, Dissertation, Johns Hopkins University (1906).

basis, then the preparation of the solutions on the latter basis must correct for the space occupied by the molecules of the dissolved substance. With the aid of the equation deduced by A. A. Noyes and referred to above, the osmotic pressures

Table XXX.—Glucose.

Normal concentration.	Osmotic pressure on weight-normal basis. ¹	Osmotic pressure on volume-normal basis, calculated.	Osmotic pressure on volume-normal basis, corrected.	Molecular O. P. on weight-normal basis.	Molecular O. P. on volume-normal basis, calculated.	Molecular O. P. on volume-normal basis, corrected.
1	2	3	4	5	6	7
0.1	2.40	2.42	2.40	23.97	24.23	23.96
0.2	4.65	4.75	4.64	23.24	23.74	23.21
0.3	7.01	7.24	7.00	23.38	24.14	23.33
0.4	9.30	9.70	9.26	23.24	24.25	23.16
0.5	11.65	12.28	11.59	23.29	24.55	23.17
0.6	14.01	14.92	13.91	23.34	24.86	23.18
0.7	16.37	17.61	16.23	23.38	25.16	23.18
0.8	18.77	20.39	18.56	23.45	25.49	23.20
0.9	21.25	23.32	20.96	23.60	25.91	23.29
1.0	23.59	26.16	23.23	23.59	26.16	23.23

Mean value of $d = 0.1125$.

obtained on the volume-normal basis have been corrected, and these are found to agree with the pressures found on the weight-normal basis.

By means of Table XXX. it is possible to compare the osmotic pressures of glucose solutions at 0° obtained on the weight-normal basis (column 2) with those obtained on the volume-normal basis (column 3) and also with the latter corrected according to van der Waals' equation (column 4). The table also contains the corresponding molecular osmotic pressures (columns 5, 6 and 7). Column 1 gives the normality of the solutions either on the weight-normal or on the volume-normal system.

Since no experimental data was at hand for the osmotic pressures on the volume-normal basis, these were calculated from the pressures found experimentally on the weight-normal basis. The volumes of the weight-normal solutions are known from their densities, and assuming that osmotic pressure is inversely proportional to the volume, it is possible to calculate

¹ See Table XXV.

what the pressures would be if the volume of the solutions were 1 liter. For example, take the 0.7 normal solution. On the weight-normal basis its volume is 1076.14 cc. and its osmotic pressure, 16.37 atmospheres. Its pressure on the volume-normal basis is obtained by the proportion,

$$1076.14 : 1000 :: x : 16.37.$$

x , the pressure on the volume-normal basis, is found to be 17.61 atmospheres.

It will be noted that the osmotic pressures thus obtained (column 3) are considerably in excess of the pressures found on the weight-normal basis. In the normal solution, the difference amounts to 2.57 atmospheres. Column 6 shows that the corresponding molecular osmotic pressures increase rapidly with the concentration, showing that the osmotic pressure on the volume-normal basis is not strictly proportional to the concentration.

For the purpose of correcting the volume-normal pressures, the value of d in the equation, $p(v-d) = K$, was calculated for each successive pair of concentrations. Thus, for p_1 , v_1 and for p_2 , v_2 in the formula,

$$d = \frac{p_2 v_2 - p_1 v_1}{p_1 - p_2},$$

were substituted the pressures and volumes of the concentrations, 0.2-0.3; 0.3-0.4; 0.4-0.5; etc. The 0.1 normal concentration was not used in the calculation since its pressure is most probably too high. The mean value of d was found to be 0.1125.

The corrected molecular osmotic pressures in column 7 were obtained by substituting in the equation, $p(v-d) = K$, for p , the pressures in column 3, for v the volumes of the solutions which contain a gram-molecular weight of the glucose, and for d the above value, 0.1125. It is to be noted that the molecular pressures thus obtained are perfectly constant. This shows that the abnormal pressures, that are obtained in concentrated solutions on the volume-normal basis, are to be explained in the same way as the deviations from Boyle's law in the case of gases.

By multiplying these molecular osmotic pressures by the

normality of the solutions, the corrected pressures on the volume normal basis in column 4 were obtained. These agree quite closely with the pressures actually found on the weight-normal basis, the latter being somewhat higher in the more concentrated solutions. This is what would be expected, since, in calculating the pressures on the volume-normal basis, the assumption was made that the pressure is inversely proportional to the volume, which is not strictly true. On the volume-normal basis the pressure increases with the concentration faster than by direct proportion. Hence, the pressures, which would be obtained experimentally on this basis, would be higher than

Table XXXI.—Cane-Sugar.

Normal concentration.	Osmotic pressure on weight-normal basis. ¹	Osmotic pressure on volume-normal basis, calculated.	Osmotic pressure on volume-normal basis, corrected.	Molecular O. P. on weight-normal basis.	Molecular O. P. on volume-normal basis, calculated.	Molecular O. P. on volume-normal basis, corrected.
1	2	3	4	5	6	7
0.1	2.44	2.49	2.44	24.40	24.90	24.43
0.2	4.80	5.00	4.80	24.00	24.99	24.02
0.3	7.16	7.60	7.16	23.87	25.34	23.87
0.4	9.40	10.17	9.40	23.50	25.43	23.50
0.5	11.85	13.07	11.83	23.70	26.14	23.65
0.6	14.25	16.01	14.21	23.75	26.68	23.69
0.7	16.81	19.24	16.70	24.01	27.49	23.86
0.8	19.33	22.51	19.10	24.16	28.13	23.86
0.9	22.13	26.19	21.68	24.59	29.10	24.09
1.0	24.78	29.88	24.20	24.78	29.88	24.20

Mean value of $d = 0.19$.

those given in column 3. So, also, the corrected pressures in column 4 should be somewhat higher.

The relations, which have just been brought out regarding the corrected osmotic pressures on the volume-normal basis and the pressures obtained on the weight-normal basis, in the case of glucose solutions at 0°, hold equally well for solutions of cane-sugar at the same temperature. This is readily seen in Table XXXI., which is entirely similar to Table XXX., except that it contains the pressures of cane-sugar solutions, while the latter contains the pressures of glucose solutions. By comparing columns 2 and 4 in this table, it is seen that the pressures on the volume-normal basis, corrected by van

¹ Am. Chem. J., 37, 459.

der Waals' equation, agree with the pressures obtained experimentally on the weight-normal basis.

This agreement between the experimental pressures (for glucose and cane-sugar) obtained on the weight-normal basis with the corrected pressures on the volume-normal basis, warrants the statement that the space occupied by the molecules of the dissolved substance can be corrected for by preparing the solutions with a fixed amount of water, that is, on the weight-normal basis.

In a strict application of van der Waals' equation to osmotic pressure, correction must be made for the volume of the molecules of the solvent. It does not appear that, by preparing the solutions on the weight-normal basis, correction is made for this. However, since on this basis, pressures are obtained which are strictly proportional to the concentration, it seems that this factor is eliminated, as it is a constant in all solutions, or else it is so small that it does not produce an effect on the osmotic pressure that can be detected.

To summarize: Since by preparing all the solutions with a fixed amount of water, pressures are obtained which are strictly proportional to the concentration, since the volume of such solutions (in the case of glucose at 0°) is practically equal to the sum of the volumes of the solvent and of the dissolved substance, and since the pressures obtained experimentally on this basis are the same as those on the volume-normal basis corrected according to van der Waals' equation, it appears that correction is made automatically, by preparing the solutions on the weight-normal basis, for the space occupied by the molecules of the dissolved substance. Also, the standard volume for osmotic pressure is to be regarded as that of the solvent in the pure state.

In calculating the theoretical gas pressures, the volume has been taken as that of the solvent at the temperature of maximum density. It seems, from what has been said, that the volume should be taken as that of the solvent at the temperature of the experiment. However, the difference in pressure, that is caused by taking the volume as that of the solvent at the temperature of maximum density, instead of at the tem-

perature of the experiment, is only 0.07 atmosphere for a normal solution at 24°, a difference in pressure far too small to be detected at present.

Some other interesting facts are brought out in Tables XXX. and XXXI. Although the osmotic pressures of glucose solutions agree approximately with the pressures of corresponding cane-sugar solutions on the weight-normal basis, the pressures differ greatly on the volume-normal basis. In the normal solution the pressure of cane-sugar is 3.72 atmospheres higher than the pressure of glucose. The corresponding solutions in each case contain the same number of molecules of the dissolved substance per unit volume, but it is clear that they are not osmotically equivalent.

This is readily explained if we consider the concentration in each case with respect to the amount of water present.

Table XXXII.

Normal concentration. 1	Ratio of number of molecules of dissolved substance to number of molecules of water in weight-normal solutions. 2	Ratio of number of molecules of glucose to number of molecules of water in volume-normal solutions. 3	Ratio of number of molecules of cane-sugar to number of molecules of water in volume-normal solutions. 4
0.1	1 : 555.6	1 : 549.2	1 : 544.1
0.2	1 : 277.8	1 : 271.4	1 : 266.3
0.3	1 : 185.2	1 : 178.8	1 : 173.8
0.4	1 : 138.9	1 : 132.5	1 : 127.5
0.5	1 : 111.1	1 : 104.7	1 : 99.7
0.6	1 : 92.6	1 : 86.2	1 : 81.2
0.7	1 : 79.4	1 : 73.0	1 : 67.9
0.8	1 : 69.5	1 : 63.1	1 : 58.0
0.9	1 : 61.7	1 : 55.3	1 : 50.4
1.0	1 : 55.6	1 : 49.2	1 : 44.1

Since the molecular volume of cane-sugar is greater than that of glucose, the cane-sugar solutions necessarily contain less water per unit volume. In this respect, also, volume-normal solutions are more concentrated than weight-normal solutions. We have seen that the osmotic pressure on the former basis is higher than on the latter (columns 2 and 3 in both tables).

The difference in concentration between weight-normal solutions and volume-normal solutions and also between volume-normal solutions of glucose and cane-sugar, in respect to the

amount of water present, is shown in Table XXXII. In column 2 is the ratio of the number of molecules of dissolved substance to the number of molecules of water in weight-normal solutions. This ratio is, of course, the same for all weight-normal solutions, irrespective of the nature of the dissolved substance. Column 3 contains the ratio of the number of molecules of glucose to the number of molecules of water in volume-normal solutions, and column 4, the same for volume-normal solutions of cane-sugar.

In column 2, it is seen that the amount of water varies inversely as the concentration in weight-normal solutions, and in these the osmotic pressure is strictly proportional to the concentration. Columns 3 and 4 show that the amount of water in volume-normal solutions is less than in the corresponding weight-normal solutions and, also, that the amount of water in these solutions does not vary inversely as the concentration. The volume-normal glucose solution is 11.6 percent more concentrated than 10 times the 0.1 normal solution, and the volume-normal cane-sugar solution is 23.4 percent more concentrated than 10 times the 0.1 normal.

Not only does the amount of water in volume-normal solutions not vary inversely as the concentration, but the amount of water is different in corresponding solutions of different substances. Thus, the 0.1 volume-normal cane-sugar solution is about 9 per cent more concentrated than the corresponding solution of glucose, and the normal solution, about 10.4 per cent more concentrated than the supposedly equivalent glucose solution.

For these reasons, it is clear why the osmotic pressure of volume-normal solutions is higher than for the corresponding weight-normal solutions, why the pressure of volume-normal solutions is not directly proportional to the concentration, and why the pressures of volume-normal solutions of different substances are different. It will be seen then, that the osmotic pressures of glucose solutions and of the corresponding solutions of cane-sugar should vary inversely as the amount of water present in these solutions. Thus, if we represent by a the relative number of molecules of water in volume-normal glucose

solutions, b the relative number of molecules of water in volume-normal cane-sugar solutions, c the osmotic pressure of the glucose solutions, and x the osmotic pressure of the cane-sugar solutions, then this proportion should hold,

$$a:b::x:c.$$

That it does hold approximately is shown in Table XXXIII.

Table XXXIII.

Volume-normal concentration.	$a.$	$b.$	$c.$	$x.$	Osmotic pressure of cane-sugar solutions.
0.1	549.2	544.1	2.42	2.44	2.49
0.2	271.4	266.3	4.75	4.88	5.00
0.3	178.8	173.8	7.24	7.45	7.60
0.4	132.5	127.5	9.70	10.08	10.17
0.5	104.7	99.7	12.28	12.90	13.07
0.6	86.2	81.2	14.92	15.84	16.01
0.7	73.0	67.9	17.61	18.93	19.24
0.8	63.1	58.0	20.39	22.18	22.51
0.9	55.3	50.4	23.32	25.59	26.19
1.0	49.2	44.1	26.16	29.19	29.88

From these considerations it is evident that the use of volume-normal solutions is not a correct method of comparing reactions in which water plays a part. Weight-normal solutions, however, contain the same number of molecules of dissolved substance and of water, no matter what the dissolved substance is. Also, weight-normal solutions, containing decimal parts of a gram-molecular weight of the dissolved substance, are exact multiples of each other in regard to the relative concentrations of the dissolved substance and of the water. For this reason, solutions prepared on this basis are to be recommended for the study of all reactions, such as hydrolysis, where the water takes part in the reaction.

BIOGRAPHY.

The author of this work, Francis M. Rogers, was born in Morganton, N. C., March 22, 1883. Since that time his home has been in Winston-Salem, N. C., in the private schools of which place he received his early education. In the Fall of 1898 he entered Guilford College, where he remained for one year. In 1899 he entered Davidson College, from which institution he received the degree of Bachelor of Arts in 1903. During the following year, he was instructor in the chemical laboratory of the above institution and at the same time pursued advanced studies in chemistry. In 1904 he received the degree of Master of Arts. In the Fall of that year he entered the chemical department of the Johns Hopkins University. His subordinate studies were physical chemistry and mathematics. During the three years of his connection with this university, he held a Hopkins Scholarship from North Carolina.

